Correction: An electric-field induced dynamical state in dispersions of charged colloidal rods

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The authors would like to address an error in the calculation of the rod–rod interaction potential $V_D$ in this paper, “The origin of an electric-field induced dynamical state in dispersions of highly charged colloidal rods”, where a mechanism is suggested and a theory is presented for a dynamical state as found experimentally in ref. 1. This error changes values of constants in the equation of motion for the orientational order parameter, but does not change any of the conclusions in the paper.

The error made is concerned with the interaction potential between two charged rods. For thick double layers the interaction potential is therefore (in the notation of our paper)

$$V_D(R, \hat{u}_1, \hat{u}_2) = \frac{\exp(kd)}{4\pi\epsilon(1 + \kappa d)} \int_{-\infty}^{\infty} dl_1 \int_{-\infty}^{\infty} dl_2 \exp\left\{ -k|l_1 \hat{u}_1 - l_2 \hat{u}_2 + r| \right\},$$

where $d$ is the rod core-diameter, $a = d/2$ the radius, $\epsilon$ the dielectric constant of the solvent, and $v_1$ and $v_2$ are the local line-charge densities at the points on the contour of the rods 1 and 2 for which the distance between the points is minimum, respectively. The minimum distance between the center lines of the two rods is equal to

$$r = R \cdot (\hat{u}_1 \times \hat{u}_2)/|\hat{u}_1 \times \hat{u}_2|,$$

where $R$ is the distance between the mid-points of the two rods. It is erroneously stated in our work that the integral cannot be evaluated explicitly. In fact this integral can be evaluated analytically, as already stated in ref. 2, and is equal to

$$\int_{-\infty}^{\infty} dl_1 \int_{-\infty}^{\infty} dl_2 \exp\left\{ -k|l_1 \hat{u}_1 - l_2 \hat{u}_2 + r| \right\} = \frac{2\pi \exp(-kr)}{\kappa |\hat{u}_1 \times \hat{u}_2|}$$

(1)

For a uniformly charged rod (without field-induced polarization) the interaction potential is therefore (in the notation of our paper, and with $\beta = 1/k_0 T$)

$$\beta V_D(R, \hat{u}_1, \hat{u}_2) = \frac{K_D}{|\hat{u}_1 \times \hat{u}_2|} \exp\left\{ -kr|R \cdot (\hat{u}_1 \times \hat{u}_2)/|\hat{u}_1 \times \hat{u}_2|\right\},$$

(2)

where the erroneous factor in $1/kr$ that we had in our paper is absent, and where (with $l_0$ the Bjerrum length),

$$K_D = \frac{2\pi Z^2 \exp(kd)}{(1 + \kappa d)^3} \frac{l_0^3}{\kappa L^2}$$

(3)

This expression for $K_D$ differs by a factor $\pi/2$ from the expression that we had in our paper. In the same way, in the potential $V_{EE}$ due to E-field induced charges in eqn (21) in our paper, the factor $1/kr$ should be omitted, while the correct value for the constant $K_E$ is also different by a factor $\pi/2$ from eqn (22) in ref. 1

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where \( \kappa_c = 2\pi l_0 \bar{c} \) is the inverse “condensate length”, with \( \bar{c} \) the number surface concentration of condensed ions in the absence of the electric field, and (with \( K_0 \) the modified Bessel function of the second kind of zeroth order),

\[
K_0 = \frac{\pi (\kappa_c / \kappa)^2 \exp(\kappa d)}{8(1 + \kappa a)^2 (1 + 2\kappa a \mathcal{K}(\kappa a))^2} \left[ 1 \right]^{1/2},
\]

(4)

Although the error made in determining the potential between two rods is admittedly quite fundamental, it has a minor effect on the equation of motion of the orientational order parameter, in the sense that it slightly changes the values of coefficients, but does not affect the structure of the equation of motion.

As a consequence of the erroneous factor \( 1/\kappa r \) in the potentials in eqn (21) and (26) in the original paper, the asymptotic behaviour of the integral,

\[
I(A) = -\kappa d + \int_0^\infty d\alpha [1 - \exp\{-A \exp\{-\alpha\}\}],
\]

(5)

needs to be evaluated instead of the similar integral, evaluated in appendix A, where \( \exp\{-\alpha\} \) is replaced by \( \exp\{-\alpha\}/\alpha \) (the extra erroneous \( 1/\alpha \) is due to the factor \( 1/\kappa r \) in the interaction potential). The asymptotic form of this integral has been evaluated in ref. 3,

\[
I(A) = -\kappa d + \ln\{A\} + \gamma_E,
\]

(6)

where \( \gamma_E = 0.5772\ldots \) is Euler’s constant. This should be compared with the incorrect result in eqn 55 in ref. 1, which reads: \( I(A) = -\kappa d + \ln\{A\} + C \), with \( C = -3/4 \). Correct results are thus obtained by simply replacing \( C \) by \( \gamma_E \) in all expressions in our paper. In particular, the effective diameter is equal to

\[
\frac{d_{\text{eff}}}{d} = \frac{1}{\kappa d} \frac{\ln\{K_0\} + \gamma_E}{},
\]

(7)

which is essentially identical to the expression given in ref. 4.

In effect, the use of an erroneous potential amounts to changing the values of the constants \( K_0 \), \( K_E \), and the expression for \( d_{\text{eff}} \) in the otherwise correct equation of motion for the orientational order parameter. A publication is in preparation where experiments at different ionic strengths as well as various rod-concentrations is compared with theory, using the correct numerical values of these parameters.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

References